

# Flightweight Carbon Nanotube Magnet Technology

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## LIST OF ACRONYMS AND SYMBOLS

AFM atomic force microscope

Al aluminum

Au gold

BSCCO bismuth-strontium-calcium-copper-oxide

CNT carbon nanotube

Cu copper

CVD chemical vapor deposition

EBID electron beam-induced deposition

EMF electromotive force

Fe iron

FIB focused ion beam

HTS high-temperature superconductor

LHe<sub>2</sub> liquid helium

LTS low-temperature superconductor

MD molecular dynamics

MFM magnetic force microscope

Mg magnesium

MgB<sub>2</sub> magnesium diboride

MHD magnetohydrodynamic

MMF magnetomotive force

# LIST OF ACRONYMS AND SYMBOLS (Continued)

MWCNT multiple-wall carbon nanotube

Nb niobium

Ni nickel

Pd palladium

Pt platiunum

RTS room-temperature superconductor

SEM scanning electron microscope

Si silicon

Sn tin

SWCNT single-wall carbon nanotube

TBCO thallium-barium-calcium-copper-oxide

TEM transmission electron microscope

Ti titanium

W tungsten

YBCO yttrium-barium-copper-oxide

#### **NOMENCLATURE**

В magnetic flux density magnetic field В critical magnetic field  $B_c$ lower critical magnetic flux density  $B_{c,1}$ upper critical magnetic flux density  $B_{c,2}$ diameter d magnetic field intensity (ampere-turn) H I current  $\boldsymbol{J}$ current density engineering current density  $J_e$ inductance  $\boldsymbol{L}$ mass m number of coil turns N R bending radius Ttemperature critical temperature  $T_c$ time t Vvoltage permeability of the media under consideration μ permeability of free space  $\mu_0$ relative permeability of the media with respect to free space  $\mu_r$ density ρ

#### TECHNICAL PUBLICATION

#### FLIGHTWEIGHT CARBON NANOTUBE MAGNET TECHNOLOGY

#### 1. INTRODUCTION

Carbon nanotubes (CNTs) hold tremendous promise as a material for manufacturing flightweight magnets and enabling envisioned future aerospace propulsion and power systems. Indeed, current research indicates that CNTs can achieve current densities at least three orders of magnitude larger than known superconductors\* and mechanical strength two orders of magnitude larger than steel. These revolutionary properties imply that the material could potentially be used to construct both the winding and the confinement structure of a magnet with dramatic reductions in size and weight in comparison to contemporary manufacturing techniques. For example, CNT strands might be directly used to wind the magnet coil, and the use of carbon-carbon composite materials made with CNT fibers could potentially reduce the weight of the containment structure by a factor of 10. If either of these manufacturing techniques can be successfully implemented, performance-to-weight ratios of advanced airborne/spaceborne systems will be greatly improved; and if both can be implemented, magnets will become an almost negligible component of total system weight.

Contemporary design concepts for lightweight magnets are based on either resistive or superconducting winding materials. <sup>1-4</sup> Resistive magnets generally use either copper (Cu) or aluminum (Al) conductors that are excited or energized by a portion of the generator output or motor power input. This approach suffers from the disadvantage that they are normally limited to relatively low fields and require a major portion of the generated power or applied power in the case of a motor. Such magnets, when designed for ground applications, will almost always utilize an iron (Fe) core to reduce the amount of power required. This is due to the large increase in permeability of Fe compared to air or free space, as observed from the fundamental relationship

$$\mathbf{B} = \mu \mathbf{H} = \mu_0 \mu_r \mathbf{H} \quad , \tag{1}$$

where **B** is the magnetic flux density, **H** is the magnetic field intensity,  $\mu$  is the permeability of the media under consideration,  $\mu_0$  is the permeability of free space, and  $\mu_r$  is the relative permeability of the media with respect to free space.

<sup>\*</sup>For the purpose of this Technical Publication, the term "superconducting" is used to mean conduction of current with very low or zero resistance. The CNT conduction process may not meet all definitions that are currently in use for superconductivity.

Values of  $\mu_r$  depend upon the temperature of the material and the magnetic flux density, but are generally well above 1,000 for good magnetic Fe. For this reason the required H (ampere-turns) to produce a given flux density is much smaller for flux densities less than  $\approx$ 2 T (20,000 G), at which point most magnetic circuit materials are at or near saturation. Beyond this level of magnetic field flux density, the relative permeability essentially becomes unity. Thus, most Earth-bound magnets have iron cores with an air gap only as large as needed since the length of the air gap is the main determinant of how many ampereturns are required to get the desired flux density. In an electric motor or generator, this air gap is quite small. For a magnetohydrodynamic (MHD) generator or accelerator, it is the minimum size to allow access for the plasma flow channel. However, the weight of iron makes it a poor choice for airborne applications except for the very smallest components. Permanent magnets have improved in performance greatly in the past few years; however, they are still only practical for very small systems with small air gaps. Thus, high-field, large-bore magnets intended for flight systems do not include any core material in the magnetic circuit even though the required number of ampere-turns is greater by at least three orders of magnitude.

Because of the resulting requirement for large values of **H** (ampere-turns), it is invariably better to use superconductor windings combined with the best structural materials available in the sense of strength-to-weight ratio. Superconductor families available can be generally characterized as follows:

- Low-temperature superconductors (LTSs) requiring refrigeration at liquid helium (LHe<sub>2</sub>) temperatures (≈4.2 K). The principal metallic LTS materials of engineering use are Nb<sub>3</sub>/Sn and Nb/Ti. LTS technology typically achieves engineering current density around 10<sup>4</sup> A/cm<sup>2</sup> when conventional conductor stabilizer (Cu or Al) is added as a quench path.
- High-temperature superconductors (HTSs) are superconducting at liquid nitrogen (LN<sub>2</sub>) temperatures (e.g., 77 K), but may require refrigeration to lower temperatures in order to achieve the desired performance in terms of critical magnetic field and/or current density. Currently, two principal families are being developed, although research has been or is being carried out on literally hundreds of materials. These are bismuth-strontium-calcium-copper-oxide (BSCCO) wire and thin-film superconductors that include yttrium-barium-copper-oxide (YBCO) and thallium-barium-calcium-copper-oxide (TBCO). The BSCCO wire is in limited commercial production and is achieving engineering current densities around 10<sup>4</sup> A/cm<sup>2</sup> at 20 K. The thin-film superconductors are still in development with a national goal of engineering current density of 10<sup>5</sup> A/cm<sup>2</sup> at 77 K.
- Room-temperature superconductors (RTSs) are also vigorously being sought. One recent development has been the carbon "buckyballs" and single-layer CNTs. Superconductivity has been demonstrated in these materials doped with alkaline metals.<sup>5</sup>
- The current state of development of the single-wall carbon nanotubes (SWCNTs) for both RTSs and for greatly improved structural composites is in its infancy; however, it is developing rapidly. Less than a year ago, production processes yielded on the order of a gram per day<sup>6–10</sup> and have advanced to kilograms per day at the time of this writing. 11 Continued progress in production capability is anticipated although techniques for purification of the CNT from the amorphous or graphitic carbon and metal catalyst particles will need further refinement. 12,13 Optimum processes for producing composite structural materials are still to be developed,

although the extremely high strength-to-weight ratio of CNT and its revolutionary impact on space system weight leaves little doubt that it can and will be done in the future. <sup>14,15</sup> A somewhat less recognized but important aspect of CNT material is the early research findings, indicating superconducting behavior. For example, doping CNT with cesium, potassium, or rubidium has been shown to produce superconductivity. <sup>16</sup> Some researchers suggest that the latter technique could lead to room temperature superconductivity. Undoubtedly, such issues will be resolved as production techniques improve and the quantity of CNT available for research increases.

In order to define the relative payoff of CNT material for flight system magnets, it is of interest to calculate the weight of the coil, warm bore tube, and stress containment structure for each of the alternative material technologies. As a baseline case for these calculations, consider a 1-m-long magnet having a 42-cm-diameter cylindrical warm bore. The weight estimation methodology assumes a warm bore thickness, calculates the required coil size, and calculates a stress containment structure needed to withstand the stresses due to magnetic forces. No allowance for cryogenic systems is included in these weights.

Figure 1 shows a plot of estimated weight for an air core magnet of the type that would be applicable to terrestrial applications. It has an engineering current density,  $J_e$ , of  $10^4$  A/cm<sup>2</sup> and uses stainless steel for the stress containment structure and warm bore. Engineering current density is the current carried by a conductor divided by the total cross-sectional area, including structure, stabilizer, insulator, etc. A fill factor is also used to designate how much of the coil volume is conductor. In these calculations, the fill factor is taken as 5, meaning that the coil conductors take up one-fifth of the coil volume. A safety factor of 4 is also used on the force containment structure, meaning the calculated stress is one-fourth the yield strength of the structure. Shown in the lower curve of figure 1 is an estimate of the weight of a magnet that uses current state-of-the-art carbon composite material. This is representative of technology that would be used to build an airborne magnet today.

The current U.S. national program targeted on the development of thin film superconductors has routinely produced small samples having current densities exceeding  $10^6$  A/cm<sup>2</sup> and has a program goal of producing commercial wire having an engineering current density of  $10^5$  A/cm<sup>2</sup>. If this technology became available, a magnet constructed using current composites would have a weight indicated by the top curve of figure 2. If an advanced composite using ultra light and strong CNTs were used for the confinement structure, the resulting magnet weight (assuming the same conductor technology) would be as shown by the lower curve for this case.

If CNTs could be developed into superconductors with the expected current-carrying capability (i.e.,  $J_e$ =10<sup>6</sup> A/cm<sup>2</sup>), the weight would be dramatically reduced, as shown in figure 2. This engineering current density is somewhat conservative given the fact that researchers have been measuring current densities on the order of 10<sup>9</sup> A/cm<sup>2</sup>, but in short, individual CNTs. The upper curve for this case represents the weight calculated for this conductor using current composite technology for the containment structure. The lower curve for this case represents the predicted performance for advanced composites using CNT fibers. It is noteworthy that a magnet of this size, which is suitable for a 10-MW MHD generator or accelerator, might ultimately weigh only a few kilograms.

#### 2. CARBON NANOTUBE TECHNOLOGY STATUS

Research on SWCNTs is progressing at a highly accelerated pace around the world because of its basic scientific value and the obvious commercial incentive. Over the past year, for example, two significant advances have been announced that lend credence to the rapid application of this technology to commercial devices. First, a new method was developed for greatly expanding the production of CNTs. Second, a collaboration between researchers at Rensselaer Polytechnic Institute and Tsinghua University, Beijing, succeeded in producing much longer bundles of SWCNTs ( $\approx$ 20 cm) than was previously available. Such rapid progress virtually renders any status review obsolete by the time it first appears in print. Nevertheless, an attempt is made here to capture the basic status of CNT technology as a starting point for examining potential magnet applications.

## 2.1 Superconductivity Attributes of Carbon Nanotubes

Carbon naontubes offer a number of attractive features with respect to superconducting coils, if indeed the early measurements yielding superconducting behavior are confirmed. First, the small size of CNTs implies that they can be used to make very small coils if a way can be found to manipulate them effectively. Second, the intrinsic tensile stiffness and strength of CNTs means that the total mass required to wind the coil and protect the coil from the large forces produced by the magnetic field can be greatly reduced. Third, the large thermal and normal state conductivity of CNTs implies that the normal metal matrix required in traditional superconducting magnet wires in order to carry the current and the heat in the case of a quench is greatly reduced, if not removed entirely. These advantages make it worthwhile to consider the possibility of using CNT-based wires to wind high-field miniature coils.

A critical issue is whether CNTs are indeed superconductors. Over the past three years, a number of groups have reported observing superconducting correlations in both individual and rope forms of SWCNTs. One of the first experiments by the Orsay group measured the temperature-dependent resistance and critical current of individual SWCNTs as well as bundles of SWCNT sandwiched between two superconducting contacts. Depending on the resistance of the device, they were able to see a transition to a low-resistance state at temperatures on the order of 1 K. The surprising aspect of their work, however, was that the critical currents in these devices were much larger ( $\approx 40$  times) than would be expected from the value of the energy gap in the superconducting electrodes. Experiments by the Stanford group also observed evidence of superconducting correlations in SWCNTs, which could be controlled by applying a voltage to a nearby gate electrode. 19

In these early experiments, it is thought that superconducting behavior was induced by the proximity of the superconducting contacts on either side of the SWCNT. More recently, however, the Orsay group has been able to observe intrinsic superconductivity in SWCNT bundles as measured between normal metal contacts.<sup>20</sup> In this case, the resistance showed a sharp drop at a temperature of 0.3 K but did not go to zero. This was due to the small residual resistance of the contacts. The critical current of these devices was 60 nA, which again is much larger than expected from traditional low-temperature theories.

Superconductivity has also been reported up to a temperature of 15 K in a matrix of individual SWCNTs having very small diameters (0.4 nm) embedded in a zeolite,<sup>21</sup> and there has been a recent report of possible superconductivity at temperatures as high as 400 K.<sup>22</sup>

The nature of superconductivity in CNTs is not theoretically understood at this time. It is known that SWCNTs are almost ideal one-dimensional conductors. But for superconductivity to exist, the electrons must have a strong short-range attractive interaction, which, it is believed, might arise from coupling to the elastic modes of the nanotube.<sup>23</sup> Therefore, one might reason that the higher transition temperature observed in arrays of individual SWCNTs is due to their smaller diameters (0.4 nm), which gives rise to stronger electron-phonon coupling. On the other hand, a truly one-dimensional system can only exhibit long-range correlations at zero temperature, and it is necessary that there be some coupling between nanotubes. Consequently, bundles of nanotubes may have higher critical temperatures and currents than individual CNTs. These results are still controversial and more experimental and theoretical work is clearly required.

Also at issue is how stress affects the transport properties of CNTs. Winding a nanotube into a tight coil need not introduce tremendous deformations of the nanotube structure, depending on the coil radius, since individual SWCNTs are relatively compliant. To date, most experiments on CNTs have been performed on individual nanotubes or ropes of nanotubes deposited flat on substrates, with very local deformations caused by manipulations with scanning probe microscopes. Mechanical deformations induced by tension, bending, or twisting, however, will likely cause local changes in the electronic structure of individual tubes, resulting in a corresponding change in their transport properties. It is possible to model the detailed elastic deformation of wrapped SWCNTs for a wide range of wrapping configurations using relatively straightforward molecular and continuum mechanics calculations, but determination of stress effects on transport properties must be determined experimentally.

#### 2.2 Fabrication of Miniature Carbon Nanotube Coils

Apart from their intrinsic electronic properties, the technological issues related to the fabrication of miniature coils from single- and multi-walled CNTs are extremely challenging. There are three major problems associated with making miniature nanotube coils: (1) Fabrication of the "former" on which the nanotubes would be wound, (2) manipulation of the CNTs in order to wind them on the former, and (3) making electrical contact to the two leads of the resulting coil.

We anticipate that such an undertaking would initially require the fabrication of coils a few microns in diameter. In this case, the formers could be fabricated using conventional lithography techniques. Circles of the appropriate diameter could be defined by electron beam lithography onto an insulating substrate. The substrate could then be etched to leave a freestanding pillar on which the CNTs would be wound. (In practice, one would of course make an array of such pillars.) For winding the nanotubes themselves, three-dimensional nanomanipulators based on small piezoelectric motors could be utilized. At present, nanomanipulators can be operated in the chamber of a scanning electron microscope (SEM) or a transmission electron microscope (TEM), enabling one to visualize and control the winding process. Later, it is anticipated that the winding process could be automated by controlling the nanomanipulators automatically with a computer.

The final and perhaps most difficult problem in constructing miniature coils is the need to make electrical contact to the two leads. After winding, one end of the CNT coil would be at the base of the insulating pillar and the other at the top. Initially, in order to test the coils, contact to the lower end of the nanotube could be made by fabricating the insulating pillars on a conducting metal film and attaching the lower end of the CNT to the film. This can be done, for example, by "welding" the nanotube to the film by means of a focused electron beam. After the lower end of the nanotube is attached, the structure is planarized, and contact to the top end is made after patterning contacts to the CNT on each individual pillar. In this way, all the coils under test would have one common electrode but could be individually tested. Later, lithographic techniques for making lower contacts to individual solenoids could be explored.

## 2.3 Superconducting Magnesium Diboride

Much excitement has been generated recently by the discovery of superconductivity in magnesium diboride (MgB₂). This common laboratory chemical shows a well-defined superconducting transition at ≈39 K.²⁴ Unlike oxide-based, high-temperature superconductors, MgB₂ is an intermetallic superconductor. Prior to MgB₂, the highest transition temperature metallic, superconductors had transition temperatures in the range of 20 K. Like the earlier metallic superconductors, MgB₂ appears to be a conventional type II superconductor.²⁵ The advantage of using MgB₂ as the basis for superconducting devices is that its constituent elements are relatively abundant and inexpensive, and MgB₂ is, in single crystal form, a very high specific strength (lightweight and strong) material. Consequently, much effort has been expended recently in attempting to enhance the superconducting properties of MgB₂.

From the point of view of making superconducting magnets from MgB2, two properties are of importance—critical current,  $J_c$ , and upper critical field,  $B_{c,2}$ . These two parameters are related in that superconductors with high  $J_c$  typically also have high  $B_{c,2}$ . In a type II superconductor, magnetic field penetration into the superconductor occurs in the form of flux lines.<sup>26</sup> Movement of these flux lines within the superconductor results in dissipation due to the Lorentz force on the charge carriers in the superconductor, leading to a reduction in the critical current. This dissipation can be reduced by introducing pinning centers for the flux lines, as has been done very successfully for conventional superconducting magnets. This is also the case for MgB<sub>2</sub>. Introduction of oxygen impurities, <sup>27</sup> or bombardment with charged ions, <sup>28</sup> which introduces defects, has been shown to appreciably increase the critical current in MgB2 films and wires. In addition, sheathing the MgB<sub>2</sub> in Fe or nickel (Ni) layers has been shown to increase the critical current.<sup>29</sup> This is believed to be due to the magnetic shielding properties of the ferromagnetic layers as well as the cryogenic stability provided by the thermal and electrical conductivity of the metal.<sup>30</sup> As with conventional superconducting wire, the method of preparation of the MgB2 is also important. Thermomechanical techniques that promote the intergrain connectivity of MgB<sub>2</sub>, such as pressing and swaging, have also been found to increase the critical current.<sup>30</sup> With a combination of such techniques, transport critical currents in the range of 2×10<sup>5</sup> A/cm<sup>2</sup> at magnetic fields of 1.5 T have been achieved, corresponding to zero field critical currents of 10<sup>6</sup> A/cm<sup>2</sup>, and estimated critical fields in the range of 15 to 30 T.<sup>31</sup> Consequently, MgB<sub>2</sub> appears to be an excellent candidate for making high-field superconducting magnets.

Given the general interest in nanoscale devices, some workers have also focused on fabricating superconducting MgB<sub>2</sub> nanowires. These wires can be fabricated, for example, by exposure of  $\approx 100$ -nm-diameter boron wires to Mg vapor. Magnetization measurements on such nanowires show a well-defined Meissner effect at  $\approx 30$  K, although detailed measurements of the transport properties have yet to be carried out.<sup>32</sup>

The metal diborides are known to be extremely stiff (modulus of order 700 GPa) materials that might also display high strength, particularly if ways can be found to grow them in single-crystal form. MgB<sub>2</sub> is already used as a low-density nanoparticle in composites to enhance strength, such as in pure Mg or in Al alloys.

While the mechanical behavior of solid MgB<sub>2</sub> wires will differ from that of SWCNTs or SWCNT bundles, the techniques outlined above for picking up and wrapping either micron-diameter or submicron-diameter MgB<sub>2</sub> wires around insulating posts should also be relevant. We suggest that concurrent study of MgB<sub>2</sub> wires and nanowires is highly relevant for applications of low-weight electromagnets for airborne/spaceborne applications.

#### 3. CONCEPTUAL MAGNET DESIGN

It is useful to develop a conceptual design for a magnet as a means of evaluating the merit and status of CNT technology for use in conductors and as a basis for composite materials for structural use. There are several types of magnet coil configurations that may be applicable to a flight system, including the following:

- Racetrack and saddle coils as normally used for linear MHD generators and accelerators (although the Russian Pamir used solenoids with linear generators).
- Toroidal coils which are used for confinement in fusion systems and energy storage.
- Solenoidal coils as typically used for disk MHD generators and some linear pulse power MHD generators. The solenoidal configuration may also turn out to be the best choice for superconducting magnetic energy storage devices as well.

In this case, a solenoid coil was selected as the basis for a conceptual design intended to evaluate the relative merits of CNT technology. Three coils of this type were used in the Russian Pamir pulse power system in which two linear MHD generator channels were sandwiched between three solenoidal coils. In fact, an established design for a conventional resistive solenoidal magnet is used as a benchmark model for conceptualizing and evaluating a CNT magnet. This will add some element of realism to the results by clarifying the advantages that can be realized with CNT technology. Although the airborne and spaceborne applications may include saddle coils and toroids, they present some computational complexity that is manageable but not needed in terms of evaluating the relative potential of CNT technology.

A cross section of the benchmark reference solenoid magnet is shown in figure 3. Here, only the larger coil is considered. The characteristics of this coil as it currently exists with Cu conductors are summarized in table 1. This coil was designed for  $LN_2$  precooling in order to reduce the Cu conductor resistance. This resistive magnet was intended only for ground testing whereas a superconducting magnet was proposed for space application. In the Cu coil, the current density, J, is the current divided by the Cu cross-sectional area,

$$J = \frac{5,000 \text{ A}}{3.175 \text{ cm} \times 3.175 \text{ cm}} = 4,960 \text{ A/cm}^2 . \tag{2}$$

Dramatically higher current densities are potentially achievable using CNTs, assuming the technology required for practical application can be developed. There have been two recent publications that measured current densities exceeding  $10^9$  A/cm<sup>2</sup>. For this conceptual design, a base current density of  $10^7$  A/cm<sup>2</sup> is proposed but this value is to be treated as a parameter in sensitivity analyses. The impact of a current density as high as  $10^9$  A/cm<sup>2</sup> is that the coil for any application under current consideration would be of almost negligible cross section. This would have a dramatic impact on the feasibility of

Table 1. Cryogenic coil characteristics.

Magnetic flux density	5 T
Conductor width/thickness	3.175 cm / 0.3175 cm
Insulation thickness	0.025 cm
Packing factor	0.77
Inside diameter	92.4 cm
Outside diameter	174.8 cm
Height	38 cm
Number of pancakes	10
Turns per pancake	120
Total turns	1,200
Design current	5,000 A
Ampere-turns	6×10 <sup>6</sup>
Weight	4,528 kg
Resistance @ 80 K	$0.0986~\Omega$
Power dissipation @ 80 K	2.475 MW

electromagnetic systems for airborne/spaceborne applications. The magnet coil to be used as the basis for this work has 10 pancakes in series, each coil consisting of 120 turns carrying 5,000 A. Thus, there are 1,200 turns carrying 5,000 A for a total magnetomotive force (MMF) of 6×10<sup>6</sup> ampere-turns. The nanotube configuration need not follow this pattern as long as it produces the same MMF; however, it is followed initially in this preliminary concept.

The required CNT conductor cross-sectional area for the 5,000-A design current scales as 5,000/J. Thus, the original Cu conductor cross-sectional area of  $1.008 \text{ cm}^2$  is scaled to  $5 \times 10^{-4} \text{ cm}^2$  for a current density of  $10^7 \text{ A/cm}^2$  and to  $5 \times 10^{-6} \text{ cm}^2$  for a current density of  $10^9 \text{ A/cm}^2$ . The diameters of SWCNTs vary somewhat but are generally in the range of 0.5 to 2 nm.<sup>33</sup> The 0.5-nm-diameter tubes have only been made in quantity inside nanopores of zeolites, and it is widely believed that such small-diameter nanotubes will be prone to oxidation upon extraction due to the higher elastic strain energy associated with a highly curved graphene sheet. At the same time, those who attempt to calculate superconductivity are suggesting that the smallest diameter tubes are the most likely to be superconducting. Therefore, the number of nanotubes required to replace one of the Cu conductors is very large. At the base current density of  $10^7 \text{ A/cm}^2$ , this requires  $2.55 \times 10^{11} \text{ 0.5-nm-diameter nanotubes}$  or  $1.59 \times 10^{10} \text{ 2-nm-diameter nanotubes}$ . In essence, a bundle of tubes in these quantities would functionally replace each Cu conductor.

Conduction across bundled nanotube boundaries needs further exploration but is apparently poor. This is unfortunate in the sense that the current may not be effectively shunted around flaws in a nanotube, and a nanotube flaw essentially becomes a defective tube for the entire length. On the other hand, this barrier to conduction may not be sufficiently high to avoid the use of insulation between turns of coils made up from groups of nanotubes. In the Cu coil, the electric potential between layers of the coil is  $\approx 8 \text{ V}$ . If the nanotube coil is superconducting, the steady-state voltage between groups of conductor that are functionally equivalent to a turn of the Cu coil would be zero; however, insulation would be required to stand off the L(dI/dt) voltage associated with rapid changes in current. The voltage to be insulated against will be determined by the time required to bring the field up or shut it down for any particular application. The trade between activation time and insulator thickness is an important design issue in that the insulation

may dwarf the nanotube conductor volume and thereby detract significantly from the desired size reductions. One promising idea in this regard is to use a layer of insulating boron nitride nanotubes on the exterior of the CNT conductor bundles.

In laying out the equivalent nanotube coil, the individual nanotubes are assumed to be cylindrical and the adjacent layers offset one-half diameter, yielding a packing factor of 0.91 within the bundle. All nanotubes are assumed to be the same size for present purposes, but more detailed analyses will require the use of statistical-based sizes and properties. The space occupied by the conductor in this bundle  $(J=10^7 \, \text{A/cm}^2 \, \text{case})$  is  $0.0005/0.91=5.49\times10^{-4} \, \text{cm}^2$ . At this point, a shape for each pancake needs to be established. Each coil pancake is arbitrarily assumed to be 1 cm in height (vertical in fig. 3) so that all 10 would be 10 cm high instead of the 38 cm for the Cu coil. The depth of each conductor bundle, given by the cross-sectional area by 1 cm, is  $5.49\times10^{-4} \, \text{cm}$ . Between each such bundle, an insulator is needed to stand off the generated voltage when current is being changed. As previously noted, this is a critical issue with respect to design compactness.

In the present analysis, the use of a 0.1-mil-  $(2.54\times10^{-4}$ -cm-) thick DuPont's Teflon® sheet is assumed. Thus, the conductor plus insulator is  $8.03\times10^{-4}$  cm thick. Also, the overall packing factor is now reduced to 0.622. For the 120 turns in each pancake, the depth of the pancake is  $120\times8.03\times10^4$  cm = $9.63\times10^{-2}$  cm. Thus, the original coil dimensions of  $41.2\times38$  cm<sup>2</sup> are reduced to  $0.0963\times10$  cm<sup>2</sup>. The issue of optimum configuration of the coils will need to be revisited frequently as additional information about the characteristics and properties of the nanotube conductors are developed and the configuration needed from a stress containment minimization viewpoint is developed.

The stress in a cylindrical containment structure is similar for both cases, but the size is significantly smaller in the nanotube coil case. With a safety factor of 2 for each, the weight of the case is reduced by more than a factor of 10 due to the coil size reduction. Support for the conductors within the coil remains to be investigated. The unique physical strength of the nanotubes is expected to aid in this function. In fact, there is a possibility that the strength of the CNT may be sufficient so that the coil can take the magnetic forces and avoid the stress containment structure altogether. Consideration of the refrigeration requirements is deferred until additional insight is gained into the operating regimes that are feasible for the conductors.

An important aspect of magnet applications is the unique strength-to-weight ratio of CNTs, particularly as related to carbon composite materials that will significantly reduce the containment structure weight. Recent measurements of the tensile strength of SWCNTs indicate a mean breaking strength of 30 GPa  $(4.35\times10^6~\text{psi})$ . This is  $\approx$ 20 times the tensile strength of stainless steel, which is the most commonly used containment structure material. Thus, a major reduction can be made in the weight of airborne/spaceborne magnets by using CNT composite materials for stress containment, even if currently available superconducting materials are used as conductors.

#### 4. TECHNOLOGY SHORTFALLS

The pursuit of CNT magnets is high-risk, high-payoff research, and several technology shortfalls can be identified. It is likely that even more issues will arise before a practical coil can ever be built and tested.

For example, the capability to manufacture CNTs in the lengths required at a cost that will permit their use in large quantities is an important technology shortfall at the present time. Although this is obviously a critical issue, the previously cited developments related to scale-up of production facilities and the general increase in achievable lengths are certainly encouraging. To wind a practical magnet with a single nanotube, the length will have to be very long (about 8×10<sup>13</sup> m to replace a Cu conductor in the prototype design coil), but the total continuous length can be reduced to any desired length if a suitable splicing technology can be developed. It also appears that bundling large numbers of parallel tubes may be feasible if the connection technology permits good connection probability. It does not matter whether there are many tubes in parallel carrying large currents in aggregate or long tubes wound into a coil with many turns having a lesser current. The requirement for a given magnetic field is for a fixed number of ampere-turns. The currently understood characteristic of the tubes is that they do not conduct well to adjacent tubes. Thus, electrical connections have to be made to each tube and the tube must be continuous without breaks to function as a satisfactory conductor.

The capability to purify the tube bundles and test them to ensure performance is also a serious issue. This follows from the discussion above to the extent that only continuous tubes with a good electrical connection can contribute to the total ampere-turns required. Furthermore, it is necessary to develop the capability to make electrical connections to the nanotubes in large numbers with reasonable reliability.

Data on electrical current-carrying capability as a function of temperature, magnetic field strength, strain, and other environmental factors is an absolute requirement. This obviously must be clarified before much progress can be made on prototypic designs and/or analyses of the economic viability of the CNT conductors for application to magnets. For all known superconductors, the criteria for a superconducting regime is that the current density be less than a critical current density,  $J_c$ , ambient magnetic field less than a critical magnetic field,  $B_c$ , and the temperature be less than a critical temperature,  $T_c$ . Furthermore, although the criteria for superconductivity is that all three of these parameters be less than their critical values, the actual current density limit is a function of the temperature and magnetic field flux density; i.e., J=J(T,B) where  $T \le T_c$  and  $B \le B_c$ , of course. The design implication of current density is that it determines the cross-sectional area of the conductor required for a given current and directly impacts the size and weight of the magnet. The impact of required operating temperature is to determine the amount and type of refrigeration required. If cooling is required, the design must include provisions for circulating coolants such as LHe2 through the coil or for conductive removal of heat using cryocoolers. Heat transfer characteristics of the CNTs will be required for designs incorporating either of these coolant methods. Additionally, information is required on the effect of strain and deformation on current density in the nanotube. The precedent of other superconductors is that any significant strain reduces the allowable current density. In the case of the CNT, the effect, if any, of distortion of the circular cross section due to interconductor forces on current density needs to be quantified.

Mechanical properties must be determined with sufficient accuracy to ensure the attainement of a reliable mechanical design. These data are also needed to permit precise evaluation of the possibility that the extraordinarily high strength of nanotubes may permit a coil structure that is self supporting; i.e., needs no containment structure. In any event, it will be necessary to determine if the individual conductors, groups of conductors, or layers of conductors require any mechanical support. The characteristics of carbon-carbon wound composite materials available for structural application will also be needed. It is assumed here that the composite strength will scale with the strength of the nanotubes used as carbon fibers.

Finally, machinery capable of handling nanotubes during manufacturing processes is a clear technological shortfall at the present time. Although there has been some manipulation of individual tubes reported in the literature, the capability to do complex operations, as will be required in the winding of a magnet coil, has not been demonstrated.

#### 5. RESEARCH AND TECHNOLOGY STRATEGY

### 5.1 Verification of Superconductivity Attributes

The principal experimental goal at this stage should be verification of the existence of superconductivity in CNTs. To do this, measuring the transport properties of SWCNTs by making electrical contacts with metallic or superconducting electrodes is recommended. For example, individual SWCNTs or ropes of SWCNTs could be placed on an oxidized silicon (Si) substrate using a nanomanipulator. The substrate could then be patterned by electron beam lithography with large-area contact pads and fiducial marks for alignment of the tubes. After the CNTs have been placed on the surface, they could be imaged by an atomic force microscope (AFM), and electrical contacts attached through an additional step of electron beam lithography. Gold electrodes are routinely fabricated on CNTs by electron beam lithography. Current technology permits a separation between the electrodes of ≈25 nm, which is consistent with the fabrication resolution of a common electron beam system, although CNT devices will probably require a separation scale of a few microns.

Previous research has shown that observation of superconductivity is critically dependent on the quality of contact between the metallic electrodes and the CNTs. Thus, different metals and superconductors (Au, Pt, and Nb) and annealing processes should be explored to improve the contact resistance between the metallic electrodes and the CNTs. It must be emphasized that experimental determination of electrical transport properties depends on measurement of resistance as a function of temperature and magnetic field and measurement of the current voltage characteristics on extremely small-scale devices. Successful experiments will clearly require highly specialized facilities and expertise.

Attempts should also be made to wind CNTs on micron-sized formers in order to create miniature solenoids, as previously described. For example, sparse arrays of cylindrical posts could be fabricated to act as the formers on which CNTs can be wound. To make the arrays, an etch mask of micron-sized holes could be defined on top of an Si substrate using electron beam lithography. A suitable metal would then be deposited on the substrate to serve as an etch mask. The electron-sensitive resist would be dissolved, and a directional reactive ion etcher would remove the Si substrate, leaving posts beneath the metallic etch-stop. The metal overlayer could be left in place, since it could be used to make metallic contacts to one end of the CNT wires.

Making contacts to both ends of the coil winding is one of the more difficult fabrication aspects of such an endeavor. For initial tests, once the technique of winding the CNTs has been established, it would be possible to fabricate the solenoid posts on a conducting metal film, which would form one contact for all the miniature coils in the array. This could be done by depositing a metal film on top of an Si substrate followed by deposition of an insulating layer of Si dioxide or Si nitride of the desired thickness. The remainder of the processing would be the same as described above, except that the metal underlayer now acts as a natural etch-stop for the reactive-ion etching process. A CNT would then be wound on a post, and the free ends welded to the top metallic layer of the post and the bottom metallic layer using an electron

beam. A conceptual schematic of the resulting solenoid is shown in figure 4. In order to test the electrical characteristics of such a coil, one could initially use a conducting AFM tip to make contact to the top metallic layer. Later on, a permanent electrical connection could be made by applying a planarizing layer and by defining leads to the top metallic electrodes using electron beam lithography. This would also enable one to quantify the magnetic field produced by the solenoid; i.e., the magnetic field generated by passing a current through the coil could be measured with a magnetic force microscope (MFM).

Similar techniques can be applied to making miniature solenoids out of MgB<sub>2</sub>. The superconducting properties of MgB<sub>2</sub> are well established; the challenge is in winding it to make small diameter coils. Although long wires of MgB<sub>2</sub> have been successfully fabricated, the material is known to be brittle. Simply taking a long wire of MgB<sub>2</sub> and attempting to wind it probably would not work. Instead, we suggest synthesizing the MgB<sub>2</sub> coils in situ by winding 100-nm B<sub>2</sub> wires on the etched insulating posts, and then exposing the device to Mg vapor. As discussed above, this is a technique that has already been used successfully to fabricate MgB<sub>2</sub> wires; the advantage is that winding the narrow B<sub>2</sub> wires is much easier.

## 5.2 Mechanical Properties, Manipulation, and Tool Development

A second major research thrust should be the development of tools, machinery, and procedures necessary to make electrical connections to the nanotubes and to manipulate the tubes into desired configurations, including the winding of a coil for experimental evaluation. As part of the fabrication process, the following technological progress should be achieved:

- Acquiring good metallic SWCNT bundles or ropes with minimum broken conductive lines and with a length between a millimeter and centimeter. An individual coil can be 1–10 μm in diameter requiring a 3- to 30-mm-long wire for solenoid with 10<sup>3</sup> turns.
- Nanowire wrapping.
- Metallic lead attachment.

The following major conductive properties should also be investigated:

- Electrical conductivity of individual SWCNT at the condition of bending.
- Electrical and thermal conductivity of SWCNT bundle and their properties in bending.
- Interwire resistance and thermal conductivity.
- Kirchhoff's rules for a bundle of one-dimensional ballistic conductors.
- Kinetic inductance, time response of highly packed bundle of one-dimensional conductors.
- CNT/metal electrode contact (interface) resistance.

To date, all experimental work has been done on CNTs deposited on substrates. Usually, an AFM is used for manipulating (rolling, bending, applying force) and at the same time imaging the configuration of the CNT and the surface topography. An example of the manipulation of individual nanotubes is shown in figures 5 and 6. The capability to pick up individual nanotube bundles, to attach them to a conductive AFM tip or to a sharp metal wire by using a variety of clamps (including conductive clamps like Al or W), and to make nanoelectromechanical measurements of them has already been demonstrated in the laboratory using the manipulator shown in figure 7. 17

However, calculations indicate that bending and twisting will cause local changes in the electronic structure of individual CNTs.<sup>35</sup> Therefore, three-dimensional manipulation of CNTs carried out inside SEMs or TEMs to image and simultaneously make electrical transport measurements is suggested. For example, the design of a nanomanipulator that will allow for integrating an Si wafer with predeposited electrical leads and etched three-dimensional posts is currently underway, as shown in the schematic of figure 7.

The nanomanipulator probes will have electrical leads and can be used for conductive measurements. This includes the ability to measure resistive (dV/dI) and conductive (dI/dV) properties as a function of coil wrapping parameters in the regime of current or voltage bias.

## 5.3 Effect of Bending and Twisting

The electrical properties of CNTs are sensitive to geometry and can be either semiconductors or metals. The effect of metals of CNTs can also modify their electronic and transport behavior. The effect of bending on nanotube strain, for example, is illustrated in figure 8. Measuring such effects for comparison to calculations is very important, and indeed some groups have already made progress. In most applications, the wire is subjected to three sources of stress: fabrication stress, magnetic stress, and thermal contraction stress. Fabrication and magnetic stress are the most relevant with respect to magnet applications.

Since the wires in bundles or ropes are usually also twisted within the strand, each wire sees alternate tensile and compressive strain. The smaller the bending diameter, the more severe the stress is acting on the ropes.

Some initial work on modeling CNT's mechanical deformation has been done already at Northwestern University. A combined continuum/molecular dynamics (MD) modeling approach has been implemented in the analysis of nanotubes filled with fullerenes and also the mechanics of twisted SWCNT bundles. Some typical modeling results are shown in figure 9. Using improved continuum/MD modeling, the mechanics of SWCNT bundles in twisted and untwisted form could be studied further, with comparison to the continuum treatments of macroscale ropes and textiles. Topics currently under investigation include effective length for load transfer, rope response after fracture of individual SWCNTs within the rope, geometry for optimal load transfer, interlayer tribology, radial deformation of individual SWCNTs, and effect of boundary conditions (type of clamping at the ends).

As seen in figure 10, SWCNTs are typically synthesized in bundle form with high conductivity along the wire and high resistance between the individual lines. Tighter packing of separate highly conductive wires has never been achieved in practice, but such an approach should be critically examined. The result could very well be a new class of electromagnets that would revolutionize motors on Earth and have high value for space applications as well. In this regard, it is useful to note that the mechanical load transfer between individual 7(10,10) SWCNT bundles having diameters of 1.36 nm when perfectly cylindrical is dramatically influenced by the introduction of a relatively small amount of twist. This is promising for electromagnet applications in that the intrinsic stiffness and strength of SWCNT bundles, when one achieves good load transfer between all of the wires (the individual SWCNTs) in the coil, may eliminate the need for a containment structure, even at very high magnetic field operation.

The authors recommend the following experimental research tasks as a first step toward realization of SWCNT electromagnets:

- Test the electrical conductivity of a single coil. These measurements should be done in situ using a nanomanipulator with the bending occurring inside the SEM. Here, measurement of resistance or conductivity (dV/dI or dI/dV at zero bias and as a function of I or V, respectively) should be carried out by the two-terminal and/or four-terminal method to achieve a low interface resistance between the electrical leads.
- Conductivity measurements of an SWCNT bundle welded to prepatterned metal electrodes on an Si substrate. These measurements should be done at temperatures from 300 K down to 0.3 K. From these measurements, it is possible to determine electrical current-carrying abilities as a function of applied voltage (*I-V* curve), wire curvature, temperature, external magnetic field, electrode material, and welding method.
- Develop a nanowrapping tool and multilayer lithography process for nanosolenoid fabrication. This development will include fabrication of an array of well-spaced insulating posts. Two different methods are proposed: (1) Plasma deep reactive etching and (2) focused ion beam-(FIB-) induced chemical vapor deposition, as shown in figure 11.
- Definitive studies should be carried out with wrapped solenoids. These measurements could be performed inside an SEM at different temperatures and *I-V* loading conditions. The magnetic field could be directly measured by a Hall probe detector and compared with that calculated from the transport measurements.

The ability to attach low electrical resistivity and high thermal conductivity leads to nanotube wires for all types of high-density current devices is a critical problem area that has yet to be fully resolved. Recent work, however, has shown some hope that such low-contact resistance leads can be made into SWCNTs.

It was shown, for example, that two-terminal resistance can be decreased by three orders of magnitude by electron-flux exposure at high dose ( $\approx$ 1 C/cm<sup>2</sup>).<sup>39</sup> Several methods have been developed to clamp nanowires onto conductive surfaces including electron beam-induced deposition (EBID) and the FIB method.<sup>40</sup> Typical results obtained with the EBID method are shown in figure 12. Using an SEM manipulator, considerable progress has been made in measuring the mechanical properties of nanostructures and the strength of the clamps. This technology should be used to carry out an intensive study of several alternative fabrication methods for making clamps, such as electrical bonding and e-beam-induced chemical decomposition. Accurate contact resistance measurements could be also developed.

A clear route to a low-contact resistance lead has been demonstrated by Dai et al., <sup>41,42</sup> who showed that a titanium (Ti) buffer layer allows for coating of the SWCNT surface with other metals such as Au, Al, Pd, and Fe. The latter four metals are nonwetting on SWCNTs, as also shown in the same study. TEM images of Ti-coated CNTs are shown in figure 13.

#### 6. CONCLUSIONS AND RECOMMENDATIONS

Virtually all plasma-based systems for advanced airborne/spaceborne propulsion and power depend upon the future availability of flightweight magnet technology. This fact is widely recognized as a technology readiness shortfall in that current technology for resistive and superconducting magnets yields system weights that tend to counteract the performance advantages normally associated with advanced plasma-based concepts. Naturally, this deficiency is perceived as a major technical risk and hampers the acceptance and ultimate development of high-payoff, high-performance propulsion systems. The development of CNTs, however, offers renewed hope that true flightweight magnets could be fabricated in the near future. This hope is based on current projections for the electrical and mechanical properties for CNTs; i.e., current density at least three orders of magnitude larger than known superconductors and mechanical strength two orders of magnitude larger than steel. As such, LyTec LLC, Northwestern University, and NASA Marshall Space Flight Center have entered into a collaborative effort of applied research on CNTs and their ultimate application to flightweight magnets for airborne/spaceborne propulsion and power systems.

A critical review of CNT technology status reveals a rapidly progressing line of research in which projected properties and applications currently exceed the definitive scientific evidence. The early findings are very promising, but this breach can only be closed through careful and rigorous scientific research. In examining the technology shortfalls and attempting to identify the most urgent research issues, particularly as they relate to potential magnet applications, the following major issues are noted: (1) Investigation and verification of mechanical and electrical properties, (2) development of tools for manipulation and fabrication on the nanoscale, (3) continuum/molecular dynamics analysis of nanotube behavior when exposed to practical bending and twisting loads, and (4) exploration of innovative magnet fabrication techniques that exploit the natural attributes of CNTs. It is recommended that these issues be immediately addressed before launching into a major technology development program since resolution of these issues will determine the scientific viability of CNT wires and ropes as a winding material and whether they can eventually be used as an integral component of a magnet containment structure.

Any of the basic mechanical and electrical property measurements can be obtained using single CNT strands, but measurements of properties under more realistic operational conditions (e.g., bending and twisting) will require the fabrication and manipulation of bundles, ropes, and coils. Thus, initial fabrication efforts should be focused on the manufacture of miniature coils. However, long-term aim should be to adapt the knowledge and techniques to the fabrication of large-scale magnets suitable for advanced aerospace propulsion and power systems.

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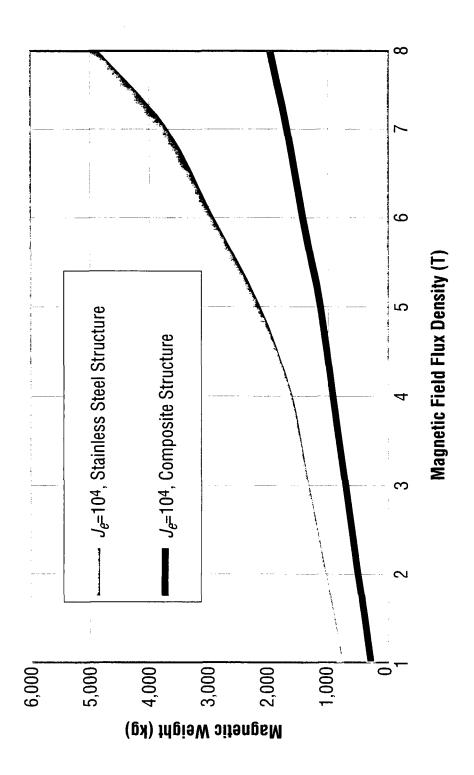


Figure 1. Comparison of magnet weight using existing technology with both a stainless steel containment structure and a composite containment structure.

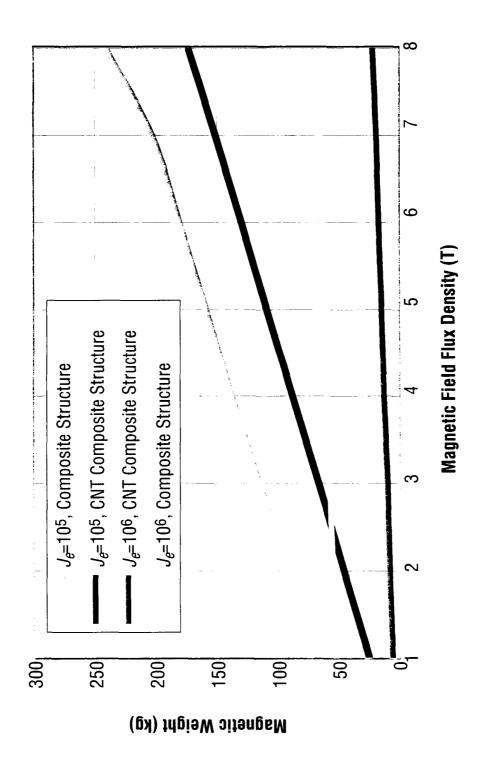


Figure 2. Magnet weight for  $J_e = 10^5 \, \text{A/cm}^2$  assuming current technology composite structure and advanced technology composite using CNTs. Also, magnet weight for  $J_e = 10^6 \, \text{A/cm}^2$ , expected engineering current density for CNT conductors, assuming both current technology composite structure and with advanced technology composites using CNTs.

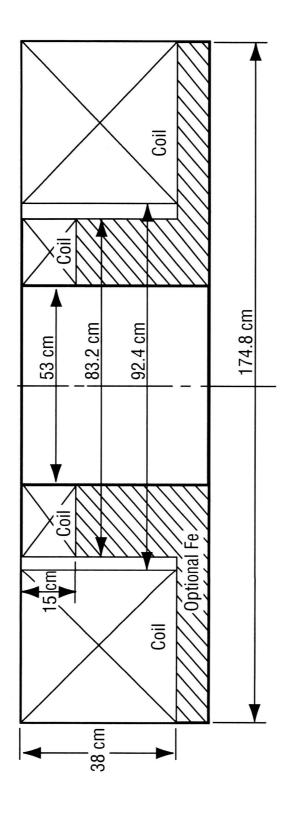


Figure 3. Solenoid resistive magnet. Referenced coil is the larger outside coil.

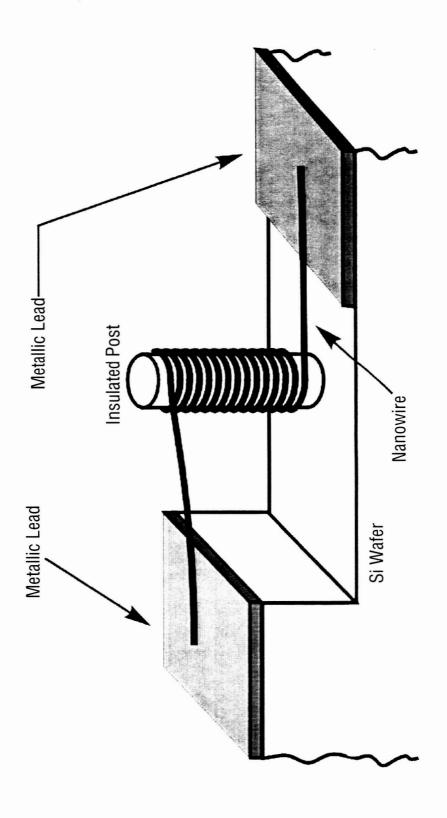


Figure 4. Schematic of nanosolenoid with wrapped wire attached to opposite electrodes.

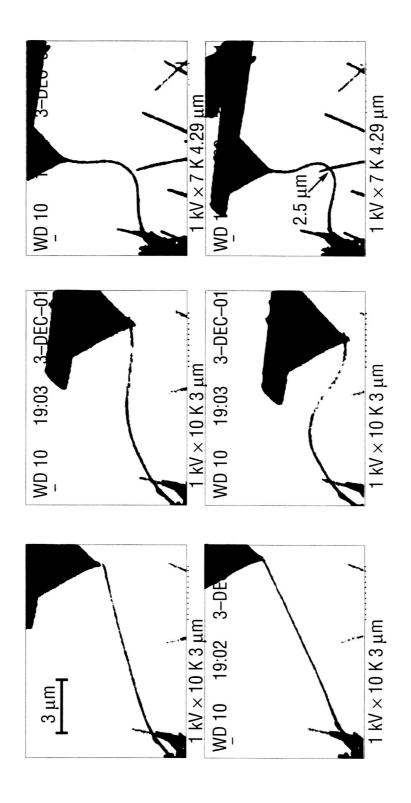
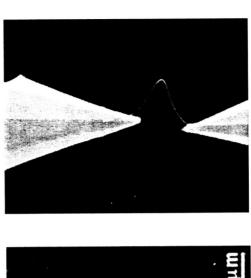


Figure 5. Manipulation of MWCNT inside of the ESM.



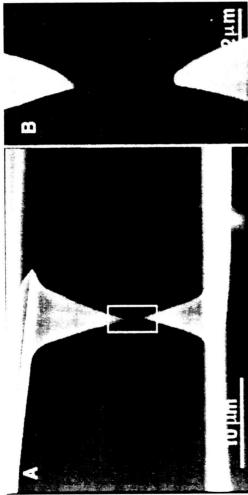


Figure 6. Individual nanotube mounted across opposing AFM cantilever tips.

Photographs labeled A and B show a tensile loading experiment.

The unlabeled photograph shows a compressive loading experiment.

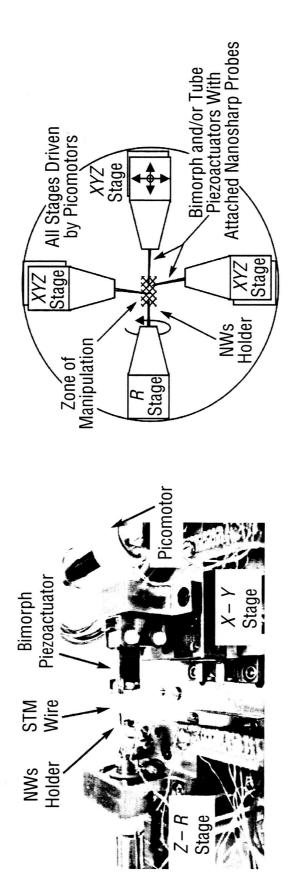


Figure 7. Existing nanopositioning stage and the design for a three-dimensional nanomanipulator.

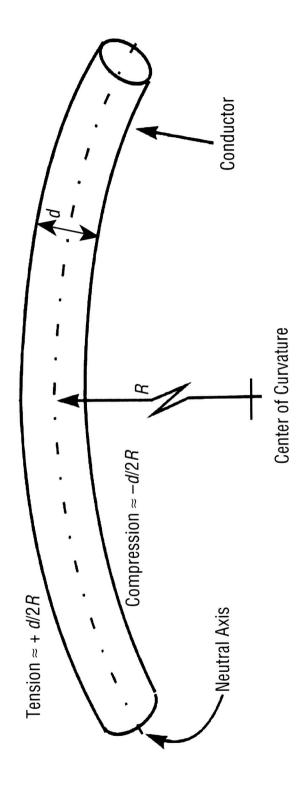


Figure 8. Illustration of bending strain introduced into a nanotube conductor. Bending strain is zero along the neutral axis.

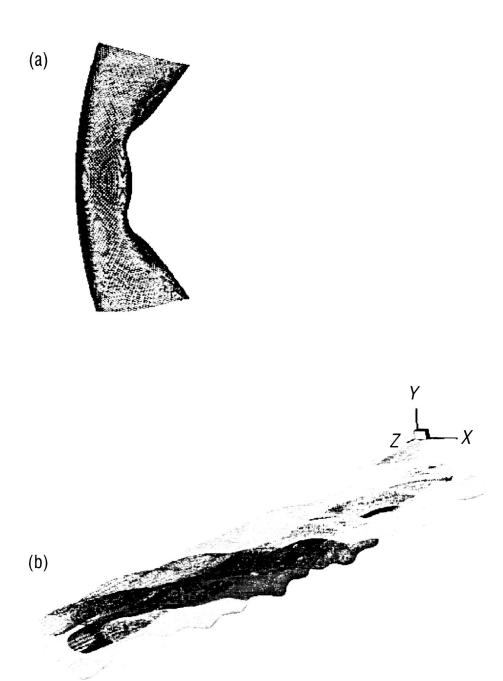


Figure 9. Continuum mechanics model of (a) a buckling SWCNT and (b) a highly twisted SWCNT bundle.



Figure 10. High-resolution TEM image of SWCNT bundle displaying the individual SWCNTs in cross section.

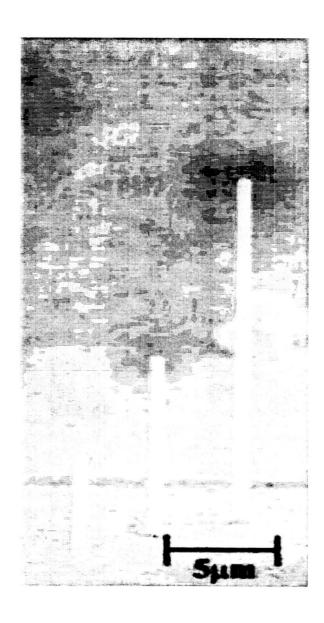


Figure 11. Diamond-like carbon pillars grown by Ga<sup>+</sup> FIB chemical vapor deposition.

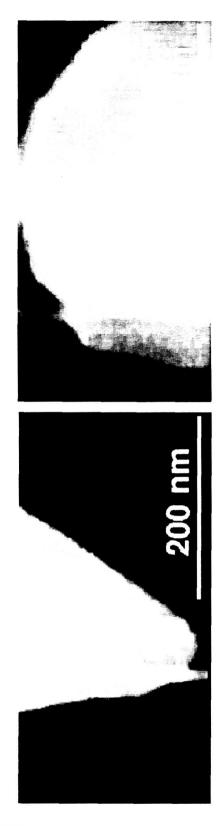


Figure 12. Closeup SEM image of an MWCNT attached to an AFM cantilever with EBID method. The carbonaceous deposit formed by EBID of residual hydrocarbons in the SEM environment acts to clamp the MWCNT specimen rigidly in place.

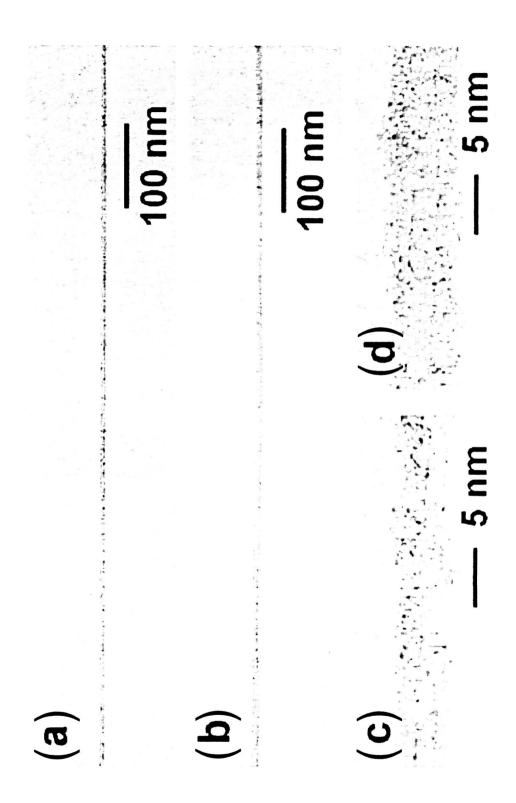


Figure 13. TEM images of Ti coating on CNTs with a nominal thickness of (a) 1 nm and (b) 2 nm; (c) and (d) are high-resolution TEM images from (a) and (b), respectively.

### REPORT DOCUMENTATION PAGE

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	Virtually all plasma-based systems for advanced airborne/spaceborne propulsion and power depend upon the future			
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magnets yields system weights that tend to counteract the performance advantages normally associated with advance plasma-based concepts. The ongoing nanotechnology revolution and the continuing development of carbon nanotube				
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availability of flightweight magnet technology. Unfortunately, current technology for resistive and superconducting magnets yields system weights that tend to counteract the performance advantages normally associated with advanced plasma-based concepts. The ongoing nanotechnology revolution and the continuing development of carbon nanotubes (CNT), however, may ultimately relieve this limitation in the near future. Projections based on recent research indicate that CNTs may achieve current densities at least three orders of magnitude larger than known superconductors and mechanical strength two orders of magnitude larger than steel. In fact, some published work suggests that CNTs are superconductors. Such attributes imply a dramatic increase in magnet performance-to-weight ratio and offer real hope for the construction of true flightweight magnets. This Technical Publication reviews the technology status of CNTs with respect to potential magnet applications and discusses potential techniques for using CNT wires and ropes as a winding material and as an integral component of the containment structure. The technology shortfalls are identified and a research and technology strategy is described that addresses the following major issues: (1) Investigation and verification of mechanical and electrical properties, (2) development of tools for manipulation and fabrication on the nanoscale, (3) continuum/molecular dynamics analysis of nanotube behavior when exposed to practical bending and twisting loads, and (4) exploration of innovative magnet fabrication techniques that exploit the natural attributes of CNTs.

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